5.3700 2209, 1282, 1273

S/079/60/030/011/007/026
B001/B066

AUTHORS: Mikhaylov, B. M. and Blokhina, A. N.

TITLE: Organoboron Compounds. LXII. Synthesis of Organoborosilicon Compounds

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp.3615-3619

TEXT: To obtain these compounds which contain boron and silicon on adjacent carbon atoms, and to study their properties, the authors synthesized such compounds by means of realkylation of triisobutyl boron with vinyl derivatives of silicon. By heating a mixture of 1 mole of triisobutyl boron and 3 moles of vinyl-methyl-diethyl silane at 130-140°C for 6 hours, tri-(2-methyl-diethyl-silyl-ethyl)-boron (I) resulted in a yield of 63%:

$$3CH_2{=}CHSiCH_3(C_2H_5)_2 + (iso\text{-}C_4H_9)_3B \xrightarrow[-3C_4H_8]{} B\left[CH_2CH_2SiCH_3(C_2H_5)_2\right]_3.$$

Compound (I) reacts, like boron trialkyls (Ref.4), smoothly with n-butyl mercaptane to give the n-butyl ester (II) of di-(2-methyl-diethyl-silyl-ethyl)-thioboric acid and methyl-trietnyl silane. Ester (II) reacts in

86501

Organoboron Compounds. LXII. Synthesis of Organoborosilicon Compounds

S/079/60/030/011/007/026
B001/B066

the cold with water, and yields di-(2-methyl-diethyl-silyl-ethyl)-boric acid (III), which can be distilled in vacuo contrary to dialkyl boric acids. Methanol gives, on action upon ester (II), not only the methyl ester (IV) expected, but also the dimethyl ester (V). The reaction of ester (II) with n-butyl alcohol proceeds in a similar way. Contrary to what was expected the esters are not converted, on boiling with alcohols, to the esters of 2-methyl-diethyl-silyl-ethyl-boric acid. Apparently, these esters are formed in that the complex compounds of esters with alcohols which result in the first stage do not only separate mercaptane to give the esters of di-(2-methyl-diethyl-silyl-ethyl)-boric acid, but are also split on the boron-carbon bond, with methyl-triethyl silane and mixed esters resulting. On excess alcohol, the latter are converted to the dimethyl esters (V) and dibutyl esters. When heating vinyl-methyl-diethoxy silane or vinyl-methyl-dichloro silane with triisobutyl boron, the compounds $[CH_2CH_2SiCH_3(OC_2H_5)_2]_3B$ and $[CH_2CH_2Si(CH_3)Cl_2]_3B$, respectively, resulted (25% yield).

T. A. Shchegoleva is mentioned. There are 7 references: 2 Soviet and 7 US.

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86501

Organoboron Compounds. LXII. Synthesis of Organoborosilicon Compounds

S/073/60/[illegible]/007/026
B001/B064

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: December 26, 1959

Card 3/3

86502

S/079/60/030/011/008/026
B001/B066

5 3700 1273, 1282, 2209

AUTHORS: Mikhaylov, B. M. and Kozminskaya, T. A.

TITLE: Organoboron Compounds. LXIII. Reactions of Esters of Alkyl Thioboric Acids With Amines

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp.3619-3624

TEXT: It was earlier found by the authors (Ref.1) that alkyl thioborates react with ammonia to give B-trialkyl derivatives of borazol, and are converted to alkyl borodiazolidines on reaction with ethylene amine. In the present paper, the above esters were reacted with amines. On the action of two moles of primary aliphatic amines, alkyl-amino groups were found to be substituted for the two alkyl-mercapto groups in esters of alkyl thioboric acids. In this connection, N-alkyl-substituted alkyl boron diamines (I) were formed according to the scheme

$$RB(SC_4H_9)_2 + 2H_2NR' \longrightarrow \underset{(I)}{RB(NHR')_2} + 2n\text{-}C_4H_9SH$$

(R = n - C_3H_7, n - C_4H_9, iso - C_5H_{11}; R' = C_2H_5, n - C_4H_9).

The reaction proceeded via complex compounds of amines with esters, which

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Organoboron Compounds. LXIII. Reactions of Esters of Alkyl Thioboric Acids With Amines

S/079/60/030/011/008/028
B001/B066

is supported by the fact that when mixing the components at -30°C in an isopentane solution, a precipitate is formed which gradually disappears. Owing to the separation of the proton from the nitrogen atom and of the anion of the alkyl-mercapto group from the boron atom, the complex compounds are converted to amino thioethers which, in turn, form complexes which decompose to mercaptane and the end product (I). On reaction of equimolecular quantities of alkyl thioborate with primary amine, probably a mixture of N-alkyl-substituted alkyl boron diamine(I), amino thioether, and the initial thioether, the separation of which was not possible, is formed. With secondary aliphatic amines, however, only one alkyl-mercapto group is substituted by the alkyl-amine radical to give organoboron compounds hitherto unknown, i.e., esters of alkyl-dialkyl-amino-thioboric acids. These compounds are stable to diethyl amine, react, however, with ethyl amine:

$$RB\begin{matrix}SC_4H_9\\ \\ N(C_2H_5)_2\end{matrix} + 2H_2NC_2H_5 \longrightarrow RB(NHC_2H_5)_2 + n\text{-}C_4H_9SH + HN(C_2H_5)_2$$

R = n-C_3H_7, iso-C_5H_{11} .

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Organoboron Compounds. LXIII. Reactions of Esters of Alkyl Thioboric Acids With Amines

S/[illegible] 008/026
B001/B060

This different behavior with respect to the two amines is obviously due to the fact that ethyl amine forms complex compounds with the esters, which are not obtained with diethyl amine. The above reamination also takes place in the reaction of ethyl amine with isoamyl-di(diethyl-amino)-boron. There are 6 references: 5 Soviet and 1 US.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: January 3, 1960

Card 3/3

P6503

5.3700 1273, 1282, 2209

B/079/60/030/011/009/026
B001/B064

AUTHORS: Mikhaylov, B. M., Arbuzov, B. M., and Grasova, L. V.

TITLE: Organoboron Compounds. LXIV. Reaction of Esters of Unsaturated Organoboric Acids With Silane Chlorides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp.3624-3628

TEXT: The authors used the addition reaction of silane chlorides to unsaturated compounds in the presence of platinum hydrochloric acid, which had been developed in the papers of Refs.1- [illegible] obtained in the present study the esters (II) and (III) by reaction of n-butyl ester of vinyl boric acid (I) with silane trichloride or methyl-silane dichloride in the presence of the above acid:

$$\underset{(I)}{CH_2{=}CHB(OC_4H_9)_2} + HSiCl_3 \longrightarrow \underset{(II)}{Cl_3SiCH_2CH_2B(OC_4H_9)_2}$$

$$\underset{(I)}{CH_2{=}CHB(OC_4H_9)_2} + CH_3SiHCl_2 \longrightarrow \underset{(III)}{Cl_2(CH_3)SiCH_2CH_2B(OC_4H_9)_2}$$

In the same way, also the n-butyl ester of allyl boric acid reacts with

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Organoboron Compounds. LXIV. Reaction of Esters of Unsaturated Organoboric Acids With Silane Chlorides

methyl-silane dichloride. According to the data of Refs.1-3, the silyl-trichloride and methyl-silyl dichloride groups add to the terminal carbon atoms. This addition takes place under milder conditions than it is the case in olefins, but it is impossible without a catalyst. In the presence of platinum hydrochloric acid, the addition of triethyl silane to the ester of allyl boric acid is far more difficult. The addition of both silanes to the esters is accompanied by side reactions which render the purification of the reaction products difficult. This applies particularly to the reaction of silane trichloride with the butyl ester of allyl boric acid. A mixture of products resulted in this reaction from which a fraction was separated which contained more chlorine than corresponds to the expected ester. Even under milder conditions no satisfactory result could be obtained. On the basis of the results obtained in the paper of Ref.4, the authors tried to carry out the addition of silane trichloride and methyl-silane dichloride to (I) and to the butyl ester of allyl boric acid under γ-irradiation. Complicated compounds resulted in this connection. After repeated distillation, a fraction was separated from the reaction products of the butyl ester of allyl boric acid with silane

Organoboron Compounds. LXIV. Reaction of Esters of Unsaturated Organoboric Acids With Silane Chlorides

S/079/60/030/011/009/026
B001/B064

trichloride, which also contained more chlorine than the ester $Cl_3Si(CH_2)_3B(OC_4H_9)$. The formation of products with higher chlorine quantities on reaction of the ester of allyl boric acid with silane trichloride in the two above-mentioned cases suggests that not only double bonds but also ester groupings play a role in the reactions of esters of unsaturated organoboric acids. To check this assumption, the following reactions were carried out: the n-butyl ester of n-propyl boric acid was reacted with silane trichloride on heating, and gave the n-butyl ester of n-propyl-chloro-boric acid and other products not identified. There are 7 references: 4 Soviet and 3 US.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: January 3, 1960

Card 3/3

11.5060
5.3700

69509

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A. S/020/60/131/04/035/073
B011/B017

TITLE: Synthesis and Some Transformations of Alkylmercaptodiboranes

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 843-846 (USSR)

TEXT: The authors studied the reaction of diborane with n-propylmercaptan and n-butylmercaptan in ether solution at room temperature and with different ratio of the reagents. Tetraalkylmercaptodiborane is formed as a main reaction product if a mercaptan excess is present (see Scheme). These compounds show considerable resistivity: they do not change on longer storage, and may be distilled under vacuum. On distilling they turn into highly viscous liquids, but some hours later they become mobile again. The molecular weight of the dimeric form of dialkylmercaptoborane is by about 1.5 times higher than the cryoscopically determined molecular weight of tetraalkylmercaptodiboranes. Apparently, a partial dissociation of the produced alkylmercapto derivatives of diborane takes place in the benzene solution. In the reaction between diborane and n-butylmercaptan (ratio 1:2), much less tetra-n-butylmercaptodiborane is formed. Di-n-butylmercaptodiborane $C_4H_9SBH_2BH_2SC_4H_9$ is formed as a main product. It is an unstable compound which is symmetrized on storing at room temperature into diborane and tetra-n-butylmercaptodiborane. The latter was identified on the basis of its capability of reacting with olefines at room temperature and of forming n-butyl ester of dialkyl-

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Synthesis and Some Transformations of Alkylmercapto-diboranes

S/020/60/131/04/035/073
B011/B017

thioboric acids (see Scheme). Furthermore, the yield in tri-n-propylboron, n-butyl ester of di-n-propylthioboric acid, and tetra-n-butylmercaptodiborane on passing propylene through the reaction mass of diborane with n-butylmercaptan is mentioned. The yield differed according to whether the mass was fresh, or stored for one night. The yield in di-n-butylmercaptodiborane is very low on the action of diborane on tetra-n-butylmercaptodiborane since equilibrium is established between the reagents and the final product (see Scheme). Polymers are known which were produced from diborane and methylmercaptan in the gas phase (Ref 2). The hydrogen atoms of tetraalkylmercaptodiboranes show much lower reactivity than diborane. Thus, the reaction of the former with mercaptan starts only at 50-60°, and proceeds energetically at the boiling temperature of mercaptan. In this connection, trialkylthioborate (see Scheme) is formed. On treating tetra-n-butylmercaptodiborane with water or alcohol at room temperature, no hydrogen is separated. Under the same conditions, N-trialkylborazols were obtained under the action of primary amines (ethylamine, n-butylamine) on tetra-n-butylmercaptodiborane. Apparently, a complex of dialkylmercaptoborane with amine (I) is formed during the first stage of the process. This complex is transformed into alkylmercaptoalkylaminoborane (II) with mercaptan being separated. An N-alkyl derivative of borazol is formed from (II) under precipitation of mercaptan. The high stability of the B-H bond becomes manifest in the reactions between tetraalkylmercaptodiboranes and olefines. The authors

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Synthesis and Some Transformations of Alkylmercapto-diboranes

S/020/60/131/04/035/073
B011/B017

succeeded in adding tetra-n-butylmercaptodiborane to olefine hydrocarbons by heating the reagents to 70° in the presence of pyridine. There are 6 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: December 22, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: December 21, 1959

Card 3/3

81722
S/020/60/133/01/33/070
B011/B003

5.3700(B)(C)

AUTHORS: Mikhaylov, B. M., Dorokhov, V. A.

TITLE: Organoboron Compounds". Reactions of 1,2-Diaryl Boranes With Olefins and Diene Hydrocarbons

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 1, pp. 119 - 122

TEXT: The authors developed a method of preparing 1,2-diaryl boranes from esters of aryl or diaryl boric acids and from diborane (Ref. 1), which makes it possible to study these diborane derivatives. Their chemical properties had been almost unknown. The authors examined the reactions of 1,2-diaryl diboranes with olefin and diene hydrocarbons: with the former, i.e., propylene or α-butylene, 1,2-diphenyl diborane enters into reaction in an ether solution on cooling. The resulting phenyl-boron dialkyls are unstable and are symmetrized to triphenyl boron and boron trialkyls already at room temperature (cf. Scheme). When triphenyl boron reacts with olefin hydrocarbons, it is possible that part of it is formed by symmetrization of the initial 1,2-diphenyl

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81722

Organoboron Compounds. Reactions of 1,2-Diaryl Boranes With Olefins and Diene Hydrocarbons

S/020/60/133/01/33/070
B011/B003

borane. Reactions with dienes were carried out in benzene or toluene solutions between -40 and -30°C. Besides 1,2-diphenyl diborane, the authors used 1,2-di-o-tolyl borane, which had been synthesized by them for the first time. A cyclic compound having a boron atom in its ring is obtained from 1,2-diphenyl diborane and butadiene in a 51% yield: 1-phenyl boron cyclopentane (I). An analogous addition of 1,2-diaryl diboranes to dienes took also place in the case of 1,2-diphenyl diborane and isoprene. This addition led to the formation of 1-phenyl-3-methyl borocyclopentane (II), whereas 1-o-tolyl borocyclopentane (III) was synthesized from 1,2-di-o-tolyl diborane and butadiene. Moreover, these conversions were accompanied by the formation of boron triaryls. This is indicative of a partial symmetrization of the used 1,2-diaryl diboranes during the reaction. 1,2-diphenyl diborane reacts with cyclopentadiene at -40°C, thus forming a solid substance which is insoluble in ether and only slightly soluble in benzene. 1-phenyl borocyclopentane had earlier been synthesized (Ref. 3) from phenyl boron difluoride and 1,4-dilithium butane (in analogy to Ref. 4). As regards the reaction of 1-aryl borocyclopentanes to active hydrogen compounds,

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Organoboron Compounds. Reactions of 1,2-Diaryl Boranes With Olefins and Diene Hydrocarbons

the authors found that 1-phenyl borocyclopentane reacts more easily with isobutyl alcohol than boron trialkyls (Ref. 5). In this case, the isobutyl ester of n-butyl-phenyl boric acid is formed under ring cleavage. Under the action of n-butyl mercaptan, 1-phenyl borocyclopentane passes over into the n-butyl ester of n-butyl-phenyl thioboric acid. This ester is the first representative of the esters of alkyl-aryl thioboric acids. There are 7 references: 3 Soviet, 1 American, 2 German, and 1 Scandinavian.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: March 9, 1960, by B. A. Kazanskiy, Academician

SUBMITTED: March 3, 1960

Card 3/3

MIKHAYLOV, B.M.

"Synthesis and Reactions of Sulpher Containing Compounds of Boron."

Report Presented at the Annual Meeting of the British Chemical Society in Liverpool. April '61

MIKHAYLOV, B.M.; KISELEV, V.G.

Radiochemical conversions of organic compounds. Neftekhimiia 1 no.2:267-273 Mr-Ap '61. (MIRA 15:2)

1. Institut organicheskoy khimii AN SSSR im. N.D. Zelinskogo.
(Radiochemistry);
(Propene) (Oxidation)

MIKHAYLOV, B.M.; GALKIN, A.F.

Synthesis and properties of B-tri-n-butymercaptoborazoles. Izv. AN SSSR. Otd. khim. nauk no.2:371-372 F '61. (MIRA 14:2)

1. Institut organicheskoy khimii im.N.D.Zelinskogo AN SSSR.
(Borazole)

20943

S/062/61/000/003/010/013
B117/B208

26.1610

AUTHORS: Mikhaylov, B. M. and Kiselev, V. G.

TITLE: Radiolytic oxidation of propylene with oxygen

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 3, 1961, 527-529

X

TEXT: In this short communication, the authors report on the oxidation of propylene with oxygen in the gaseous phase. Experiments were conducted under the following conditions: voltage of the accelerating field 120 kv; output amperage 0.1 ma (total dose $0.55 \cdot 10^{23}$ ev); initial pressure equal to atmospheric pressure, room temperature, ratio of the components 1:1 Oxidation took place in an aluminum chamber of 2 l capacity The total amount of acids was determined by titration with phenolphthaleine as the indicator; the end point was indistinct owing to the presence of peroxides The peroxides were determined iodometrically. There was no propylene oxide in the oxidation products. Gaseous oxidation products were chromatographed CO_2 and oxygen were determined by the absorption method. The results of

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Radiolytic oxidation of propylene ..

these experiments are summarized in the table. The data indicate that the main products which form during oxidation of propylene under the action of fast electrons in the gaseous phase are peroxides, acetol, carbon monoxide, and propanal. The absence of acrolein indicates that the methyl group is not oxidized. The high acetol yield may be best explained by addition of the oxygen molecule to the double bond of propylene, and by isomerization of the cyclic peroxide resulting in this way. Propanal is presumably formed by reaction of primary active propylene peroxide with initial propylene. The high carbon monoxide yield indicates that it is no decomposition product of formic acid, but one of the primary products formed in addition to the acid. The scheme of radiolytic oxidation of propylene is thus, in essential, analogous to the scheme suggested in Ref 1 (B. M. Mikhaylov, V. G. Kiselev, Izv. AN SSSR, Otd khim n. 1960, 1613) for the oxidation of ethylene under the action of fast electrons:

$$C_3H_6 \xrightarrow{\sim\!\!\!\!\!\!\int} C_3H_6^* \qquad C_3H_6^* \xrightarrow{O_2} C_3H_6O_2$$

$$C_3H_6O_2 \rightarrow CH_3COCH_2OH; \qquad C_3H_6O_2 \xrightarrow{C_3H_6} 2C_2H_5CHO.$$

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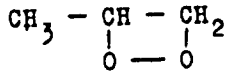
S/062/61/000/003/010/013
B117/B208

Radiolytic oxidation of propylene...

The peroxide denoted in the scheme by $C_3H_6O_2$ is assumed to have the following structure



i.e., it is a homolog of the cyclic ethylene peroxide. There are 1 table and 12 references: 2 Soviet-bloc and 10 non-Soviet-bloc.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, Academy of Sciences USSR)

SUBMITTED: August 2, 1960

Card 3/3

20945

S/062/61/000/003/012/014
B117/B208

S 2400

AUTHORS: Mikhaylov, B. M. and Vasil'yev, L. S

TITLE: New method of synthesizing alkyl boric acid esters

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no 3, 1961, 531-532

TEXT: In this "Letter to the Editor", the authors report that they have found a new method of synthesizing alkyl boric acid esters while studying the properties of tetraalkyl diboranes obtained previously (Ref 1: B. M. Mikhaylov, A. A. Akhnazaryan, L. S. Vasil'yev, Dokl. AN SSSR 136, 828, 1961). Tetraalkyl diboranes were found to react with orthoborates slowly at room temperature and quickly when heated (80°-100°C), giving alkyl boric acid esters (80-90 % yield).

$$R_4B_2H_2 + 2(R'O)_3B \longrightarrow 3RB(OR')_2 + 1/2\ R_2B_2H_4 \quad (1)$$

R = n-C_3H_7, n - C_4H_9; R' = CH_3, n-C_3H_7, n - C_7H_{15}

Reaction (1) proceeds via several stages, alkyl and alkoxyl groups being substituted for the hydrogen in tetraalkyl boranes and their primary

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S/062/61/000/003/012/013
B117/B208

New method of synthesizing alkyl...

conversion products. It was further found that dialkyl diboranes react with trialkyl borines (particularly readily when heated) to give tetraalkyl diboranes: $R_2B_2H_4 + 2R_3B \longrightarrow 2R_4B_2H_2$ The possibility of converting dialkyl diboranes resulting from reaction (1) into tetraalkyl diboranes in the presence of trialkyl borines permitted the synthesis of alkyl boric acid esters from trialkyl borines and ortho-borates under the action of catalytic amounts of tetraalkyl diboranes. In this way, various alkyl boric acid esters were obtained by heating the above components up to 80°-100°C (80-90 % yield) $R_3B + 2(R'O)_3B \xrightarrow{R_5B_2H_2} 3RB(OR')_2$ Abstracter's note: This is a full translation from the original There is 1 Soviet-bloc reference.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, Academy of Sciences USSR)

SUBMITTED: January 16, 1961

Card 2/2

MIKHAYLOV, B.M.; SHCHEGOLEVA, T.A.; SHASHKOVA, Ye.M.

Synthesis of alkylthioboric acid esters from trialkylborines and thioborates. Izv.AN SSSR.Otd.khim.nauk no.5:916-917 My '61. (MIRA 14:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boric acid) (Boron compounds)

SHCHEGOLEVA, T.A.; SHASHKOVA, Ye.M.; MIKHAYLOV, B.M.

Reactions of triethylthioborate with amines. Izv.AN SSSR.Otd.khim. nauk no.5:918-919 My '61. (MIRA 14:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boric acid) (Amines)

MIKHAYLOV, B.M.; ARONOVICH, P.M.

Decomposition of butyl esters of α,β-dibromoethylboric and β,γ-dibromopropylboric acids. Izv.AN SSSR.Otd.khim.nauk no.5: 927-929 My '61. (MIRA 14:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boric acid) (Butyl borate)

MIKHAYLOV, B.M.; SHCHEGOLEVA, T.A.

Synthesis of 1-n-butylmercaptoboracycloalkanes. Izv.AN SSSR.Otd. khim.nauk no.6:1142-1144 Je '61. (MIRA 14:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Cycloalkanes)

MIKHAYLOV, B.M.; TUTORSKAYA, F.B.

Action of amines and ammonia on triallylboron. Izv.AN SSSR.Otd. khim.nauk no.6:1158-1159 Je '61. (MIRA 14:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boron organic compounds) (Amines) (Ammonia)

25047
S/062/61/000/006/009/010
B118/B220

15.8150

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A., Shashkova, Ye. M., Sheludyakov, V. D.

TITLE: Polymers and trimers of alkyl mercapto-boranes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 6, 1961, 1163

TEXT: The authors stated that the reaction of diborane with mercaptans (1:2) in ether results in polymer alkyl mercapto-boranes. The diborane reacts with methyl mercaptan, forming a solid polymer $(CH_3SBH_2)_x$ which had been synthesized previously by A.Burg and R. Wagner (see below) without the use of a solvent. On reaction of ethyl mercaptan or n-butyl mercaptan with diborane, glass-like polymers of ethyl mercapto-borane $(C_2H_5SBH_2)_x$ or of n-butyl mercapto-borane $(n\text{-}C_4H_9SBH_2)_x$ are obtained after elimination of the ether by distillation. The polymers of ethyl mercapto-borane and n-butyl mercapto-borane are converted gradually at room temperature to the corresponding trimers of alkyl mercapto-borane.

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25047
S/062/61/000/006/009/010
B118/B220

Polymers and trimers of alkyl...

The trimer of ethyl mercapto-borane $(C_2H_5SBH_2)_3$ has the following constants: boiling at 94-96°C (1 mm Hg); $d_4^{20} = 0.9772$; $n_D^{20} = 1.5323$; data obtained: H_{act} 2.98; 2.90; B 14.37 %; 14.27 %; molecular weight (determined cryoscopically): 217.8; 220.2. The trimer of n-butyl mercapto-borane decomposes on vacuum distillation: $d_4^{20} = 0.9376$; $n_D^{20} = 1.5130$; data obtained: H_{act} 2.17; 2.15; B 10.23; 10.32 %; molecular weight: 293.3; 294.9 corresponding to $(C_4H_9SBH_2)_3$. The solid polymer of methyl mercapto-borane is stable; however, when it is dissolved in tetrahydrofuran, it is converted to the trimer of methyl mercapto-borane: boiling at 80-81°C (1.5 mm Hg); $d_4^{20} = 1.0121$; $n_D^{20} = 1.5483$; data obtained: H_{act} 3.46; 3.37; B 17.80; 17.30 %; molecular weight: 182.5; 183.6 corresponding to $(CH_3SBH_2)_3$. The trimers of alkyl mercapto-boranes are fairly stable against the action of air and water. There is 1 non-Soviet-

Card 2/3

25047
S/062/61/000/006/009/010
B118/B220

Polymers and trimers of alkyl...

bloc reference. The reference to the English-language publication reads as follows: A. Burg, R. Wagner, J. Amer. Chem. Soc. 76, 3307 (1954).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy USSR)

SUBMITTED: April 20, 1961

Card 3/3

MIKHAYLOV, B.M.; LOROKHOV, V.A.

Synthesis of N-trialkylborazines from alkylamine boron hydrides in the presence of mercaptans. Izv. AN SSSR. Otd.khim.nauk no. 7:1346-1348 Jl '61. (MIRA 14:7)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Borazine)

29523

S/062/61/000/011/012/012
B103/B147

5.3700

AUTHORS: Mikhaylov, B. M., and Dorokhov, V. A.

TITLE: Synthesis of some dialkyl-amino boranes and alkyl-mercapto (dialkyl-amino) boranes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 11, 1961, 2084 - 2086

TEXT: The following compounds were synthesized: (a) n-propyl-mercapto (dimethyl-amino) borane (boiling point 48 - 50°C at 13 mm Hg; d_4^{20} - 0.8706; n_D^{20} - 1.4701); (b) n-butyl-mercapto (dimethyl-amino) borane (boiling point 55 - 57°C at 7 mm Hg; d_4^{20} - 0.8666; n_D^{20} - 1.4669); (c) n-propyl-mercapto (diisoamyl-amino) borane (boiling point 92 - 94°C at 1.5 mm Hg; d_4^{20} - 0.8422; n_D^{20} - 1.4640); and (d) n-butyl-mercapto (piperidino) borane (boiling point 73 - 74°C at 1.5 mm Hg; d_4^{20} - 0.9170; n_D^{20} - 1.4944). The initial substances were dialkyl-amino boranes: (e) dimethyl-amino borane;

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B103/B147

Synthesis of some dialkyl-amino..

(f) diisoamyl-amino borane; and (g) piperidine borane with yields close to the theoretical values. The reaction used for the synthesis of e) - g) has previously been described by the authors (Dokl. AN SSSR, 135, 1961); Zh. obshch. khimii, 31, 7384 (1961)). It permits the synthesis of different alkyl-mercapto (dialkyl-amino) boranes from borane complexes with secondary amines. e) - g) were obtained by passing diborane at low temperatures through an ether solution of the relevant secondary amine. An easy method of synthesizing dialkyl-amino boranes consists in reacting lithium boron hydride with the hydrochlorides of the amines in ether medium. a) - d) were synthesized by allowing the relevant mercaptans to act on e) - g) at 100 - 120°C as follows:

$$R_2NH\,BH_3 + R'SH \longrightarrow R_2NB\begin{matrix}SR'\\H\end{matrix} + 2H_2$$

a) - d) exist in a monomeric form. They can be hydrolyzed and are oxidized in air. They react with alcohols at room temperature while separating H_2. Their alkyl-mercapto groups are substituted by an alkyl-amino or dialkyl amino group under the effect of primary or secondary amines. On heating with higher mercaptans, a) - d) exchange their RS

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29523
S/[illegible]/61/[illegible]/011/[illegible]/012
B103/B147

Synthesis of some dialkyl-amino...

groups for a higher alkyl-mercapto group. When heated with an excess of a higher secondary amine, both the alkyl-mercapto and the dialkyl-amino groups are substituted. Finally, data on infrared and Raman spectra of b) are presented. There are 5 references: 2 Soviet and 3 non-Soviet. The reference to the English-language publication reads as follows: A. Burg, C. Good, Inorgan. Nucl. Chem. 2, 237 (1956).

ASSOCIATION: Institut [illegible] (Institute [illegible]

SUBMITTED: [illegible]

Card 2/2

MIKHAYLOV, B.M.; VASIL'YEV, L.S.

Exchange reactions between boric organoboric acid esters and their thio analogs. Izv.AN SSSR.Otd.khim.nauk no.11:2101-2102 N '61. (MIRA 14:11)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boric acid) (Boron compounds)

23766
S/190/61/003/006/009/019
B110/B208

11.2219 also 2209

AUTHORS: Mikhaylov, B. M., Aronovich, P. M.

TITLE: Organoboron compounds. LXXVII. Polymerization of the butyl ester of vinylboric acid

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 861 - 864

TEXT: H. Normant, J. Braun (Compt. rend. 248, 828, 1959) found that vinylboric acid derivatives were capable of spontaneous polymerization. Studying some reactions of the butyl ester of vinylboric acid the authors observed a spontaneous polymerization of the ester. To investigate the properties of the polymers, the butyl ester of vinylboric acid was polymerized under the action of dry air at room temperature in the presence of the dinitrile of , '-azoisobutyric acid. Polymerization proceeded quickly under heat evolution. The resultant gel which was insoluble in organic solvents was transformed into a solid substance after exposure to air. Its analysis was not possible. The empirical composition of the polymer exposed to air was $(C_{12}H_{3\cdot}{}_{3}{}_{13}B_4)_n$. This is assumed to be a
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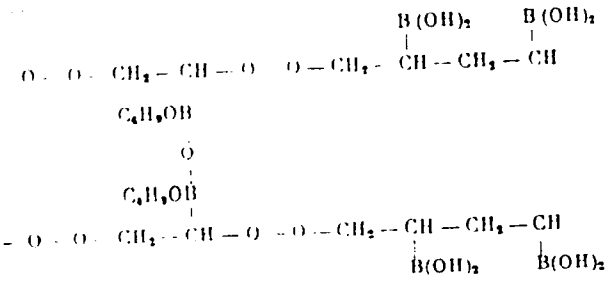
S/190/61/003/006/009/019
B110/B208

Organoboron compounds ...

trimeric copolymer of the partly hydrolyzed ester of vinylboric acid and oxygen, probably having the following structure:



I

When treated with boiling water boric acid and a new polymer with a ~4% boron content are formed. The C-B bonds along the principal chain, which have no part in the building-up of cross-links are destroyed, and the resistance to heat is considerably increased. The mass obtained in nitrogen atmosphere is more mobile than that formed in oxygen atmosphere. The

23766
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B110/B208

Organoboron compounds ...

gel is slowly dissolved in benzene. When diluted with isopentane, a hard polymer is separated. It is warmed in exposure to air, darkens, and contains ~10% more oxygen [illegible] elimate analysis than that separated in nitrogen atmosphere. Addition of the dinitrile of α,α'-azoisobutyric acid as an initiator accelerates polymerization. A low amount of impurities in the initial ester essentially influences the polymerization process. The n-butyl ester of vinylboric acid copolymerizes with styrene to $(C_{20}H_{22}O_2B_2)_n$ and with vinylbutyl ether to $(C_6H_{13}OB)_n$. By passing air into 5 g butyl ester for 3 min, the latter was heated and converted to a thick transparent gel. 2 ml dissolute benzene were added. After standing for 2 weeks, the gel swelled, the transparent liquid was decanted, and the polymer was allowed to stand [illegible] at room temperature. Solid crumbs are formed which gave 5.9 g of a [illegible] powder (78% of the initial ester), when triturated. The polymer is soluble in benzene, acetone alcohol, dioxane, and boiling chloroform. It turns yellow when heated beyond 120°C, and softens [illegible]. 1 g polymer was heated for 30 min in 5 ml of distilled water. The residue was filtered, washed out with water and dried in vacuum at room temperature. 0.05 g of a

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23766

S [illegible]
B[illegible]/B206

Organoboron compounds ...

yellow powder were obtained. Found [illegible] from the analysis: $(C_{26}H_{40}O_9B_2)_n$. The p[illegible] colors at ~210°C and darkens [illegible] dinitrile of α,α'-azoisobutyric acid were allowed to stand in N_2 atmosphere in a sealed ampul for 7 days at room temperature, then heated for 25 hr at 40°C, for 25 hr at 60°C and for 50 hr on the boiling water bath. 10 ml absolute benzene were added to the resultant gel. After addition of 100 ml isopentane the solution divided and separated a flocculent precipitate which was filtered after 1 day and dried in vacuo. Colorless powder in 21.8% yield. Formula obtained by the analysis $(C_{14}H_{26}O_{11}B_4)_n$. The polymer is insoluble in benzene, [illegible] and softens at ~200°C. When exposed to air, it becomes warm and darkens. After exposure to air for 3 days the composition was $C_{14}H_{16}O_{13}B_4$. A mixture of 5.76 g (0.02 mole) butyl ester and 1.5 g ([illegible] mole) vinylethyl ester and 0.05 g dinitrile of α,α'-azoisobutyric acid was heated after standing for 1 days in a sealed ampul, for 50 hr at 40°C, for 5 hr at 60°C, and for 25 hr on the boiling water bath; the viscosity increased within the first 50 hr. 50 ml

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Organoboron compounds ...

isopentane were added after dissolution in 3 ml benzene Formula assumed: $(C_7H_{13}O_3B)_n$. The polymer was not soluble in benzene, darkened as $>120^{\circ}C$, and softened at $\sim 180^{\circ}C$. In the copolymerization of the n-butyl ester of vinylboric acid with styrene a colorless, powder resulted in a 20% yield; it was insoluble in alcohol, acetone, benzene, dioxane and boiling chloroform: $(C_{20}H_{32}O_7B_2)_n$. There are 8 references: 3 Soviet-bloc and 5 non-Soviet-bloc. The references to English-language publications read as follows: Ref 5: R. L. Letsinger, S. B. Hamilton, J. Amer. Chem. Soc., 81, 3009, 1959. Ref 6: W. J. Lennarz, H. R. Snyder, J. Amer. Chem. Soc. 82, 2169, 1960. Ref 8: A. A. Miller, F. R. Mayo, J. Amer. Chem. Soc., 78, 1023, 1956.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: July 28, 1960

Card 5/5

MIKHAYLOV, B.M.; FEDOTOV, N.S.

Structure of complex compounds of diphenyl boron chlorides with primary amines. Izv.AN SSSR.Otd.khim.nauk no.10:1913 O '61. (MIRA 14:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boron compounds) (Amines)

88482

S/079/61/031/001/014/025
B001/B066

5.3600

AUTHORS: Mikhaylov, B. M. and Bubnov, Yu. N.

TITLE: Organoboron Compounds. LXV. Synthesis of Dialkyl Thioborates by Reaction of Mercaptans With Trialkyl Borines

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 160 - 166

TEXT: In addition to Refs. 1 - 6, the present paper describes the reactions of trialkyl borines with ethanethiol, 1-propanethiol, and thiophenol, the conversions of dialkyl thioborates by alcohols and higher mercaptans, and the reactions of trialkyl borines with alcohols in the presence of catalytic amounts of mercaptans. The reaction of ethanethiol, or 1-propanethiol with ethyl or tripropyl borines gives the corresponding dialkyl thioborates (I), and saturated hydrocarbons according to the equation:

$$R_3B + R'SH \longrightarrow \left[R_3B \longleftarrow S\begin{matrix} R' \\ H \end{matrix} \right] \longrightarrow \underset{(I)}{R_2BSR'} + RH$$

$R = C_2H_5$, n - C_3H_7 $R' = C_2H_5$, n - C_3H_7.

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Organoboron Compounds. LXV. Synthesis of Dialkyl Thioborates by Reaction of Mercaptans With Trialkyl Borines

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B001/B066

The reaction sets in at room temperature with further spontaneous heating. Short heating between 110 and 160° is necessary to ensure completeness of the reaction. Addition of mercaptan to trialkyl borine heated to 150° yields hydrogen (10 %), and unsaturated hydrocarbon (Ref. 1). The reaction of thiophenol with tri-n-butyl borine giving the phenyl ester of di-n-butyl thioboric acid, develops like the reaction with tri-n-propyl borine (Ref. 1), which yields not only a saturated hydrocarbon (n-butane) but also considerable quantities of an unsaturated hydrocarbon (butylene), and hydrogen

$$(n - C_4H_9)_3B + C_6H_5SH \longrightarrow (n - C_4H_9)_2BC_6H_5 + n - C_4H_{10} + C_4H_8 + H_2.$$

The formation of gaseous products of different compositions in the reaction of trialkyl borines with compounds having a mobile hydrogen atom (mercaptans and thiophenol) is explained by the reaction mechanism suggested in Ref. 1. Further interpretations are given in the present paper. The dialkyl thioborates are converted to dialkyl borates by heating with alcohols (Ref. 4). With higher mercaptans, dialkyl thioborates are subject to ester interchange. The synthesis of dialkyl borates from tri-

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B001/B066

Organoboron Compounds. LXV. Synthesis of Dialkyl Thioborates by Reaction of Mercaptans With Trialkyl Borines

alkyl borines and alcohols was found to take place with high yields also when mercaptan catalysts are used. In this way, e. g. the n-butyl ester of di-n-butylboric acid, and the methyl ester of di-n-propylboric acid were synthesized from the corresponding trialkyl borine and alcohol. There are 12 references: 11 Soviet, 1 US, and 1 British.

ASSOCIATION: Institut organicheskoy khimii (Institute of Organic Chemistry)

SUBMITTED: February 1, 1960

X

Card 3/3

S/079/61/031/001/015/025
B001/B066

AUTHORS: Povarov, L. S. and Mikhaylov, B. M.

TITLE: Polyene Compounds. XIV. Synthesis of Monoarylated Polyene Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 167 - 170

TEXT: The authors synthesized the following monoarylated, luminescent polyene hydrocarbons which have so far not been described: 2,6-dimethyl-1-phenyl heptatriene-1,3,5 (I), 8-methyl-1-phenyl nonatetraene-1,3,5,7 (II), and 4,8-dimethyl-1-phenyl nonatetraene-1,3,5,7 (III). They were obtained by a method described in Ref. 3, which utilized the condensation products of the acetal of methyl croton aldehyde with isopropenyl ethyl ether and ethoxy dienes (Refs. 4, 5). 4-ethoxy-6-methyl hepten-5-one-2 (IV) resulted from the ketal of 4-ethoxy-6-methyl hepten-5-one-2 (Ref. 4) on hydrolysis. On condensation with benzyl magnesium chloride, (IV) gave 4-ethoxy-2,6-dimethyl-1-phenyl hepten-5-ol-2 (V) which was converted to 2,6-dimethyl-1-phenyl heptatriene-1,3,5 (I) by boiling with HBr in aqueous alcoholic solution. The corresponding aldehydes (VI) and (VII) were obtained in the

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Polyene Compounds. XIV. Synthesis of Mono-arylated Polyene Hydrocarbons

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B001/B066

same way from the acetals of 5-ethoxy-7-methyl-octadien-2,6-al-1 and 5-ethoxy-3,7-dimethyl-octadien-2,6-al-1 (Ref. 5). 6-ethoxy-8-methyl-1-phenyl nonadien-3,7-ol-2 (VIII), and, respectively, 6-ethoxy-4,8-dimethyl-1-phenyl nonadien-3,7-ol-2 (IX) were separated on condensation with benzyl magnesium chloride; they were converted to hydrocarbons (II) and (III) by splitting off water and alcohol. In the crystalline state, compound (I) shows in ultraviolet light a pale-violet luminescence which does not appear in solution. Polyenes (II) and (III) show a bright blue luminescence, when dissolved, and do not luminesce at all in the solid state. The labile compounds (I) - (III) are oxidized even by atmospheric oxygen. Heating in dissolved state transforms them into oily products which renders their purification by crystallization difficult. There are 6 references: 4 Soviet, 1 US, and 1 British.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: March 27, 1960

Card 2/2

89517
S/079/61/031/002/010/019
B118/B208

5.3700

AUTHORS: Mikhaylov, B. M. and Vaver, V. A.

TITLE: Organoboron compounds. LXVII. Reactions of trialkyl borines with organic acids

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 2, 1961, 574-577

TEXT: Following their previous paper (Ref. 1) on the effect of compounds having a mobile hydrogen atom (water, alcohols, phenols, amines, mercaptans, thiophenol) on trialkyl borines, which gives compounds of type (I), and saturated hydrocarbons and H_2 ($R_3B + HYR' \longrightarrow R_2BYR' + RH + R_{-H} + H_2$ (Y = O, NH, S; R' = H or a carbon radical), the authors now investigated the conversions of trialkyl borines on reaction with organic acdis. Except for the reaction of acetic acid with triethyl borine giving diethyl boro acetic anhydride and ethane carried out by H. Meerwein, H. Sönke (Ref. 2), no further reactions of this type have been described. The experiments made by these two scientists were repeated, and their data confirmed at equimolecular quantities of the initial products. When the equimolecular quantity

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Organoboron compounds. LXVII. ...

of acetic acid is doubled, ethyl pyro-boro acetic anhydride is formed via the monoacetate. The formation of the latter is explained by the fact that the monoacetate is converted to ethylyl boro acetic anhydride two molecules of which split off one molecule of acetic anhydride. The synthesis of mixed anhydrides of organopyro-boric and organic acids had been carried out earlier by N. S. Fedotov and T. A. Shchegoleva (Refs. 3-5). Also the higher trialkyl borines react with acetic acid, even at room temperature, with spontaneous heating to 50-60°C; further heating of the reaction mixture between 60 and 100° soon completes the reaction. Contrary to triethyl borine, the higher trialkyl borines react with acetic acid to give the corresponding alkyl pyro-boro acetic anhydrides. At excess acetic acid, n-butyl pyro-boro acetic anhydride (V, R = n - C_4H_9) or isobutyl pyro-boro acetic anhydride (V, R = iso - C_4H_9) result after separation of two moles of the saturated hydrocarbon, and in subsequent distillation of the reaction mixture (Refs. 4, 5):

(V).

89517

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B118/B208

Organoboron compounds. LXVII. ...

On reaction of chloro acetic acid with tri-n-butyl borine, the anhydrides of n-butyl boric and chloro acetic acids and n-butane result. There are 5 references: 4 Soviet-bloc.

SUBMITTED: March 14, 1960

Card 3/3

89518

S/079/61/031/002/011/019
B118/B208

S 3700

AUTHORS: Mikhaylov, B. M. and Bubnov, Yu. N.

TITLE: Organoboron compounds. LXVIII. Dialkyl borine amines and their N-substituted compounds

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 2, 1961, 577-582

TEXT: In the present study, dialkyl borine amines and their N-substituted derivatives were synthesized from dialkyl thioborates. The thioborates react with ammonia (Refs. 1 and 2) in a strongly exothermic manner, even on cooling and separate out, at the beginning, a crystalline complex compound $R_2BSR' \cdot NH_3$ (I) which decomposes at about 20°C, and splits off mercaptan to give dialkyl borine amine (II):

$$R_2BSR' + NH_3 \longrightarrow \underset{\text{(I)}}{R_2B(SR')(NH_3)} \longrightarrow R_2BNH_2 + R'SH.$$

Complex (I) could not

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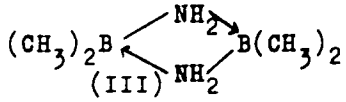
Organoboron compounds. LXVIII. ...

be obtained in pure condition, but there is no doubt about its formation. The synthesis of higher dialkyl borine amines from trialkyl borines and ammonia in the presence of mercaptans, as well as the reaction of NH_3 with dialkyl thioborates at room temperature, suggested by the authors in Ref. 4, are the most convenient methods of synthesis in preparative respects, owing to the easily accessible initial compounds. R. B. Booth, C. A. Kraus (Ref. 6) obtained, on reaction of ammonia with di-n-butyl boron chloride in the presence of Na, a product boiling at 100°C (0.01 mm Hg) which was assigned the structure of di-n-butyl borine amine. The di-n-butyl borine amine earlier synthesized by the authors (Ref. 1) boils, however, at 55.5°C (11 mm Hg), and corresponds to the structure R_2BNH_2, as was confirmed by exact chemical conversions of the dialkyl borine amines. Thus, so far only the first member of the dialkyl borine amine series, dimethyl boro amine, has been known in the form of its dimer (III)



(III)

(Refs. 3, 4, 5, 8). On the basis of molecular weight determination, the higher dialkyl borine amines are found to be monomers.

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89515

S/079/61/031/002/011/019
B118/B208

Organoboron compounds. LXVIII. ...

Dialkyl borine amines are very reactive (inflammation on the air, easy hydrolysis, reaction with alcohols) (Ref. 9). Dialkyl borine amines undergo reamination with substituted amines to give N-substituted dialkyl borine amines (Ref. 2). The latter may also be obtained easily by reaction of primary and secondary amines with thioethers R_2BSR' (Ref. 1). The most convenient method of synthesizing N-substituted dialkyl borine amines rests upon the reaction of trialkyl borines with amines in the presence of a mercaptan as a catalyst. On addition of diethyl amine to tri-n-propyl borine containing 1-propanethiol, di-n-propyl-diethyl-amino boron (VIII) was obtained in a 92% yield

$$(n.\text{-}C_3H_7)_3B + n.\text{-}C_3H_7SH \longrightarrow \underset{(VII)}{(n.\text{-}C_3H_7)_2BSC_3H_7\text{-}n.} + C_3H_8$$

$$(n.\text{-}C_3H_7)_2BSC_3H_7\text{-}n. + (C_2H_5)_2NH \longrightarrow n.\text{-}C_3H_7SH + \underset{(VIII)}{(n.\text{-}C_3H_7)_2BN(C_2H_5)_2}$$

When carrying out this reaction, the order of the addition of mercaptan and amine to the trialkyl borine is of great importance (the authors give exact instructions). The methods of synthesizing N-substituted dialkyl borine amines hitherto described in publications (Refs. 1, 3, 6, 10-15) are finally

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89518
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B118/B208

Organoboron compounds. LXVIII. ...

explained. There are 15 references: 3 Soviet-bloc and 5 non-Soviet-bloc.

SUBMITTED: March 2, 1960

Card 4/4

S/079/61/031/011/015/015
D228/D305

3700

AUTHORS: Mikhaylov, B. M., and Dorokhov, V. A.

TITLE: Alkylmercapto-(diethylamino)-boranes

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 11, 1961, 3750-3756

TEXT: Previous research by B. M. Mikhaylov and V. A. Dorokhov (Ref. 1: Dokl. AN SSSR, 136, 356, 1961) disclosed the existence of a new class of organoboron compounds--the alkylmercapto-(dialkylamino)-boranes (I). The present work is devoted to the study of three more such substances: ethylmercapto-(diethylamino)-borane -- $Et_2NBHSEt$ (II); phenylmercapto-(diethylamino)-borane -- $Et_2NBHSPh$ (III); and n-butylmercapto-(diethylamino)-borane -- $Et_2NBHSBu\text{-}n$ (IV). II($b.p.$ 65 - 75°) was prepared by distilling a solution of diethylaminoborane which was preheated at 100 - 110° for 4 hr. during the dropwise addition of diethylamine. III ($b.p.$ 82 - 84°) was obtained by distilling a mixture of diethylaminoborane and thiophenol that had first been heated at the same temperature for 1 hr

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D228/D305

Alkylmercapto-(diethylamino)-boranes

The physical properties of II, III, and IV indicate their occurrence in a monomeric form. By studying the reactions of I, the authors exposed the relative mobility of the alkylmercapto and diethylamino groups bonded to the boron atom. Thus, the butylmercapto group in IV may be replaced by an arylamino group when treating this compound with aniline or o toluidine at fairly low temperatures; similarly, the diethylamino group and not hydrogen—is replaced when III is treated with aniline at 60 - 80°. In this connection, the authors note that V. I Mikheyeva and Ye M. Fedneva (Ref. 5: ZhNKh, 2, 604, 1957) also synthesized a compound with the composition $(PhNH)_2BH$ from diborane and aniline. For the reactions of I with aliphatic amines, however, the conditions are different On boiling a mixture of IV and diethylamine for 5 hr., only half of the former substance is converted into bis-diethylaminoborane - a compound which the authors prepared, too, by slowly adding diethylamine to a solution of diethylaminoborane at a temperature of 130 - 150°. The comparative inertness of the hydrogen atom in I is further illustrated by the fact that it cannot be replaced by an alkylmercapto groups even when such com

S/079/61/031/011/[illegible]/[illegible]

Alkylmercapto-(diethylamino)-boranes D228/D305

pounds are heated with mercaptan at 200°. In the case of the higher mercaptans, the lower mercapto group is replaced by the higher. [illegible] reacts with n-butylmercaptan to form IV and ethylmercaptan. The reactions between I and alcohol are believed to proceed first through the introduction of the alkylmercapto and diethylamino groups, after which the dialkoxyborane either acts directly on the alcohol to give hydrogen or else is symmetrized into orthoborate and diborane when the latter reacts with the alcohol. The low mobility of the hydrogen atom bonded to boron is also displayed by the inability of I to combine with unsaturated hydrocarbons - even at 120° in the presence of pyridine. The introduction of boron and its derivatives is best accomplished if the electron shell of the B-H bond is relatively dense. According to their tendency to react with unsaturated compounds the various derivatives of [illegible] placed in the following series: RBH$_2$, R$_2$BH, (R$_2$N)BH, (R$_2$N)$_2$BH. There are 12 references [illegible]

The reference to the English language publication reads as follows: Burg, E. Randolph, J. Am. Chem. Soc. 73, 953 (1951).

Card 3/3 Submitted Dec 1960

31191
S/079/61/031/012/005/011
D227/D301

S 2410

AUTHORS: Mikhaylov, B. M., and Dorokhov, V. A.

TITLE: Organoboron compounds. LXXXVII. The action of diborane on the aryl derivatives of boron

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4020-4023

TEXT: When diborane is reacted with esters of aryl- and diaryl boric acids, 1,2-diaryl diboranes are formed, according to the following reactions:

$$6ArB(OR)_2 + 2B_2H_6 \rightleftarrows 3(ArBH_2)_2 + 4(RO)_3B \quad (1)$$

$$3Ar_2BOR + 2B_2H_6 \rightleftarrows 3(ArBH_2)_2 + B(OR)_3 \quad (2)$$

In the case of mono-aryl acid esters the yields are low and about 20-25% of an unreacted ester is recovered, due to the back reaction

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Organoboron compounds. ...

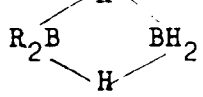
and preferential displacement of the equilibrium to the left. In the second reaction the quantity of boric acid ester obtained is 4 times less and, therefore, it proceeds more readily to the right giving higher yields of diaryl diborane. The mechanism of the former reaction is assumed to be based on the fact that the exchange of groups between aryl and alkoxyl derivatives of boron takes place through the formation of bridged compounds given by electron deficient atoms (B-H-B and B-O-B), followed by decomposition of the

R

dimers. The mechanism of the latter reaction consists of two stages, initial substitution of the alkoxy group with hydrogen and formation of diaryl borane (in dimeric form) and alkoxyborane followed by the reaction between the former and diborane to give diaryl borane. An attempt to isolate diaryl borane (reacting diborane with n-butyl diphenyl borate) was not successful as the latter converts to triaryl boron which reacts smoothly with diborane to give diaryl

Card 2/4

Organoboron compounds. ...

diborane. In this reaction the structure  occurs, in

which B-R-B bond is formed with the utilization of the carbon sp^3-orbital and two sp^3-orbitals of the boron atoms. In the experimental part 1,2-diphenyl diborane was reacted with n-butyl orthoborate, in ether, by stirring the two compounds at 30-35°C for 5 hours. After the removal of diborane the product yielded, on distillation, di-n-butyl phenyl borate (b.pt. 106-110°C/3mm), n-butyl orthoborate, n-butyl diphenyl borate and triphenyl boron. Diphenyl diborane was prepared by passing diborane through n-butyl diphenyl borate in hexane. When an excess of ester was used triphenyl boron was first formed, (m.p. 137-145°C), which reacted with diborane in ethereal solution to give 1,2-diphenyl diborane, m.pt. 82-85°C. 1,2-Diphenyl diborane was also prepared by passing diborane through an ethereal solution of diphenyl borochloride, and the yield corresponded to 60%. There are 3 references: 2 Soviet-bloc and 1 non-

Card 3/4

Organoboron compounds. ...

Soviet-bloc. The reference to the English-language publication reads as follows: E. Eberhardt, B. Crawford, W. Lipscomb, J. Chem. Phys. 22, 989, (1954).

SUBMITTED: January 6, 1961

Card 4/4

89616

S/020/61/136/002/022/034
B016/B060

5.3700

AUTHORS: Mikhaylov, B. M. and Dorokhov, V. A.

TITLE: Organoboron Compounds. Complex Compounds of Borane and Phenyl Borane With Diethyl Amine and Some of Their Conversions

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 2, pp. 356-359

TEXT: It has been noted that a 90% yield of diethyl amine borane (I) is obtained by the reaction between diethyl amine and diborane in ethereal medium: $2(C_2H_5)_2NH + B_2H_6 \rightarrow 2(C_2H_5)_2NH \cdot BH_3$ (I). In contrast with data of Ref. 1, I is no crystalline substance, but a colorless liquid which is distillable in vacuum and is stable to water and alcohols at room temperature. A similar behavior is displayed toward diethyl amine by 1,2-diphenyl diborane which is smoothly converted into diethyl amine phenyl borane $(C_2H_5)_2NH \cdot H_2BC_6H_5$ (II). The latter is less heat-resistant than I. I and II are associated in benzolic solution and certainly more strongly

Card 1/3

Organoboron Compounds. Complex Compounds of Borane and Phenyl Borane With Diethyl Amine and Some of Their Conversions

S/020/61/136/002/022/034
B016/B060

so in the liquid state. At 130-150°C, I separates hydrogen to give rise smoothly to bis-(diethyl amino)-diborane $[(C_2H_5)_2NBH_2]_2$ (III), a crystalline substance that undergoes sublimation in vacuum. III reacts with water and alcohols from 60°C on. At 90-150°C, II is converted in vacuum to a diphenyl diethyl amino boron $(C_6H_5)_2BN(C_2H_5)_2$ mixture (V) and diethyl amino borane (VI). At -70°C, VI gives rise to a mobile liquid, which, when heated, dimerizes to crystalline III under heat evolution and hydrogen separation. The first stage of the pyrolytic process is believed to give rise to phenyl diethyl amino borane

$C_6H_5B\begin{matrix}H\\ \diagdown\\ N(C_2H_5)_2\end{matrix}$ (IV), which is subsequently symmetrized to V and VI. The symmetrization is reversible. Pyrolysis of II under atmospheric pressure leads, beside V, to the formation of a fraction which violently reacts with alcohol under hydrogen separation. The same fraction results on heating of V and VI. The authors believe this fraction to be IV with an admixture of III. III and n-butyl mercaptan at 100°C give rise t. n-butyl

89616

Organoboron Compounds. Complex Compounds of Borane and Phenyl Borane With Diethyl Amine and Some of Their Conversions

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mercapto (diethyl amino)-borane constituting a novel type of a substituted borane: $(C_2H_5)_2NB\langle^{SC_4H_9\text{-}n}_{H}$ (VIIa). Alkyl mercapto-(diethyl amino)-boranes (VII) can be produced in an 85% yield directly by the action of mercaptans upon diethyl amino borane at 100°C. This process probably has the following course: a) a complex of diethyl amine with alkyl mercapto borane (VIII) is formed with hydrogen separation; b) VIII is converted into a complex of diethyl amino borane with mercaptan (IX); c) VII results from IX under hydrogen separation. VII is a liquid with an unpleasant odor which readily oxidizes in the air and is distilled in vacuum in undecomposed state. As it is a monomer it reacts with alcohols violently under hydrogen separation. As contrasting therewith, dimers do not react with alcohols at room temperature. III adds to olefins in the presence of pyridine at 120-130°C. Di-n-butyl diethyl amino boron (IXa) and Di-n-octyl-diethyl amino boron (IXb) are formed in this manner, though not readily and in lesser yields. There are 6 references: 3 Soviet, 1 US, and 1 German.

Card 3/3

Inst Org. Chem in N. D. Zelinskiy AS USSR

88406

S/020/61/136/004/014/026
B016/B075

11.1240

AUTHORS: Mikhaylov, B. M., Akhnazaryan, A. A., and Vasil'yev, L. S.

TITLE: Synthesis and Properties of Tetra-n-propyl Diborane and Tetra-n-butyl Diborane

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 4, pp. 828 - 831

TEXT: The authors studied the reaction of diborane with tri-n-propyl boron and tri-n-butyl boron in etheric solution, and determined the following facts: 1) When passing 1 mole of diborane through a 4-mole solution of boron trialkyl at room temperature, tetraalkyl diboranes are produced in a yield of 70-85%, i.e., tetra-n-propyl or tetra-n-butyl diborane. 2) When using an equimolecular quantity of diborane, an asymmetric di-n-propyl diborane is isolated by distilling the reaction products. The second synthesis method is based on the reaction between diborane and olefins (Ref.4). This reaction is catalyzed by different ethers. Reaction of diborane with propylene-1 and butene-1 (ratio 1 : 4) at -70 to -30°C in an etheric medium resulted in a 48% yield of tetraalkyl diboranes. The latter

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Synthesis and Properties of Tetra-n-propyl Diborane and Tetra-n-butyl Diborane

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are completely stable up to 100°C and can be distilled in vacuo. In benzene solution they are partly dissociated into dialkyl borane. Tetra-alkyl diboranes spontaneously inflame in the open air. They are highly reactive and react with alcohols under the formation of dialkyl boric acid esters. With aniline they form dialkyl phenyl amino boron. Under the action of mercaptans, tetraalkyl diboranes are converted to dialkylthio-boric acid. Such reactions are convenient preparation methods for synthesizing organoboron compounds, since only small quantities of side-products are formed. Tetra-n-butyl diboranes more difficultly react with glycol. In this case, almost equal quantities of glycol esters of di-n-butyl boron and n-butyl boric acid are formed, and, in addition, tri-n-butyl boron. From the formation of the latter, the following was concluded: The action of nucleophilic reagents causes a substitution of hydrogen atoms by tetraalkyl diboranes, and also a disproportionation of tetraalkyl diboranes into boron trialkyls and alkyl boranes. Under the action of a nucleophilic reagent, the alkyl borane thus forming results in an organoboron compound with a radical on the boron atom. On the other hand, boron trialkyl remains either unchanged (e.g., in the reaction with glycol), or enters into reaction and, e.g., with mercaptan, forms an

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Synthesis and Properties of Tetra-n-propyl Diborane and Tetra-n-butyl Diborane

S/020/61/136/004/014/026
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ester of dialkyl thioboric acid (Ref.6). In the latter case, hydrogen as well as a small quantity of propane are present in the gaseous reaction products. Asymmetric boron trialkyls can be synthesized by reacting tetra-alkyl diboranes with olefins. There are 12 references: 6 Soviet and 4 US.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, Academy of Sciences USSR)

PRESENTED: July 9, 1960, by B. A. Kazanskiy, Academician

SUBMITTED: July 6, 1960

Card 3/3

5.2410

AUTHORS: Mikhaylov, B. M., and Vasil'yev, L. S.

TITLE: Reactions of diborane and alkyl boranes with esters of boric and alkyl boric acids and with the [illegible]

PERIODICAL: Akademiya nauk SSSR. Doklady [illegible]

TEXT: B. M. Mikhaylov in cooperation with V. A. Dorokhov (Ref. 1: DAN, 130, 782, (1960)) continued the studies of diborane and stated that diborane forms with dialkyl boric esters besides the expected tetraalkyl diboranes alkyl boric esters in place of boric esters, aldehydes and ethers

$$8R_2BOR' + B_2H_6 \rightarrow 4RB(OR')_2 + 2RBH_2 + 2R_2BH$$

In the opinion of the authors, this has the following mechanism of formation of the primary reaction: The hydrogen atom is detached from the diborane molecule and, thus, alkyl-alkoxy boranes and alkyl boranes are formed

$$R_2BOR' + BH_3 \rightarrow RB(H)(OR') + RBH_2$$

This [illegible] boric ester and alkyl borane: $RB(H)(OR') \rightarrow RB(H)_2 + RBH_2$ and

Card 1/6

25782

Reactions of diborane and alkyl

(3) are only diagrammat

they proceed with partic

(see diagram). Alkyl

part with dialkyl

atom: $R_2BOR' + RBH \rightarrow RB(H)OR + R_2BH$

borane dimerizing

is converted according

direction of the primary

ester is replaced by a hydrogen atom

dialkyl borane and alkoxy borane

Moreover, the authors

$R_2BOR' + R'OBH_2 \rightarrow 2RB(H)OR' + RBH_2$

$R'OBH_2 \rightarrow 1/3\ R'O_3B + 1/3\ BH_3$

decomposed to orthoborates and

dialkoxy borane).

Card 2/6

Reactions of diborane and alkyl ...

by fractionating the reaction products. Consequently, also this initial direction of reaction results in the formation of the same final products according to (5) as well as to (3) and (4). Orthoborates react with tetraalkyl diboranes. According to (9) alkyl boric esters are formed slowly at room temperature and rapidly at 60-100°C with a yield of about 80%: $(R_2BH)_2 + 2(R'O)_3B \rightarrow 3RB(OR')_2 + (RBH_2)_2$ (9). In this case, the initial stage is based on the substitution of a hydrogen atom in tetraalkyl borane for an alkoxyl group: $R_2BH + (R'O)_3B \rightarrow R_2BOR + (R'O)_2BH$ (10). The further conversions of the dialkyl boric esters and dialkyl diboranes (10) are analogous to those in (6)-(8) and (5)-(5), an alkyl boric ester and an alkyl borane being formed. The reactions (1)-(10) are reversible. This is proved by: $3(R_2BH)_2 + 4RB(OR')_2 \rightleftharpoons 8R_2BOR + B_2H_6$ (11), where $R = n\text{-}C_3H_7$, $R' = CH_3$. Also the conversion of dialkyl diborane to diborane and tetraalkyl diborane is reversible. $2R_2B_2H_4 \rightleftharpoons R_4B_2H_2 + B_2H_6$ (12). For this reason, the reaction proceeds on boiling of tetraalkyl diborane with orthoborate not according to (9) but to

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Reactions of diborane and alkyl [illegible]

$3\ (R_2BH)_2 + 8\ (R'O)_3B \longrightarrow 6RB(OR')_2 + B_2H_6$ (13). Thus 100% diborane referred to (13) were isolated after 2 hr of boiling tetra-n-propyl diborane and methyl borate. On distillation of the reaction products, 80% of n-propyl boric dimethyl ester was obtained. Moreover, it was stated that dialkyl diboranes form tetraalkyl diboranes, with boron trialkyls. The tetraalkyl diboranes were used in catalytic quantities in the reactions between boron trialkyls, orthoborates and alkyl boric esters (14) and (16)(see preliminary communication of the authors Ref. 6. Izv. AN SSSR, OKhN, 1961, No. 5, 857). At about 200°C esters either of alkyl or of dialkyl boric acids are formed dependent on the character of the alkyl group in the boron trialkyl. High yields of the esters mentioned (70-80%) are obtained even at 60-100°C by using the catalyst mentioned for diborane, its alkyl, alkoxyl and alkyl mercapto derivatives:

$$R_3B + 2\ (R'O) \xrightarrow{(R_2BH)_2} 3RB(OR')_2$$ (14). (14) finally takes the form of (9) so that tetraalkyl diborane catalyzes the process and is regenerated continuously. Likewise, esters of dialkyl boric acids are converted to those of alkyl boric acids with a yield of 70-80%.

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Reactions of diborane and alkyl

$R_2BOR' + (R'O)_3B \xrightarrow{(R_2BH)_2} 2RB(OR')_2$ (15). Also in this case, first of all dialkyloxy borane is formed which converts the dialkyl boric esters to alkyl boric esters either directly (in analogy to (6) and (9)) or passing the stage of decomposition into diborane and orthoborate (in analogy to (8) and (1)). Thereby, tetraalkyl diborane is regenerated. Finally a reverse conversion of the esters is possible: dialkyl boric acid can be formed from an equimolar mixture boron trialkyl - alkyl boric ester by the above mentioned catalysis:

$R_3B + RB(OR')_2 \xrightarrow{(R_2BH)_2} 2R_2BOR$ (16). The yield in esters amounts to 50-70%. (1), (15), and (16) are simple in preparative respect and there are not known any other reactions giving the same results. The sulfur analogs of the orthoborates and the esters of the acids mentioned behave similarly.

$2(RS)_3B + R_3B \xrightarrow{(R_2BH)_2} 3RB(SR)_2$ (17), where R = n-C_4H_9. A small amount of n-butyl thioboric-n-butyl ester was isolated as by-product. This reaction requires more severe conditions than that with other esters. For example,

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S/020/61/139/002/012/019
B103/B220

Reactions of diborane and alkyl ...

mercapto-diborane is a more stable compound than dialkoxy borane and (in analogy to (8), decomposes easily to diborane and orthoborate. It is concluded from this fact that not dialkoxy borane but diborane reacts in those reactions where dialkoxy boranes are involved and exchange their hydrogen atom against the alkyl group at low temperatures. There are 7 references: 4 Soviet-bloc and 3 non-Soviet-bloc. The two references to English-language publications read as follows: A. E. Borer, H. I. Schlesinger (Ref. 2: J. Am. Chem. Soc., 75, 4080 (1953); W. E. ... R. Thomas (Ref. 4: Am. pat. 2835693 (1958)).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

PRESENTED: March 28, 1961 by B. A. Kazanskiy, Academician

SUBMITTED: March 22, 1961

Card 6/6

33977

S/062/62/000 002 002 0 7
B117/B138

5.2410

AUTHORS: Miknaylov B M., and Kozminskaya, T K

TITLE: Organoboron compounds 90. Organoalkoxy thioboric acid esters

PERIODICAL: Akad-miya nauk SSSR. Izvestiya Otdeleniye khimicheskikh nauk no. 2. 1962. 256-260

TEXT: This is in continuation of a study of the reaction of alkyl boron dihalides with mercaptans (Communication 89 had been published in the Izv. AN SSSR, Otd. khim. n. 1961, 2101). If a mixture of alkyl boron dichlorides and ethyl mercaptan excess is heated to boiling point, ethyl esters of alkyl chloro thioboric acid will be obtained in addition to diethyl esters of alkyl thioboric acid. The former are products of an incomplete substitution of chlorine atoms and represent a hitherto unknown type of boron compounds: $RBCl_2 \xrightarrow{C_2H_5SH} RB(SC_2H_5)_2 + RB(SC_2H_5)Cl$. R = n-$C_3H_7$; i-$C_3H_7$; n-$C_4H_9$. The yields of alkyl chloro thioboric acid

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S/062/62/000/002/001/017
B117/B138

Organoboron compounds..

esters are low even in the case of an equimolecular ratio of reagents because these esters are thermally unstable. When distilled in vacuo they are frequently decomposed into alkyl thioboric acid esters and alkyl boron dichlorides. Alkyl boron dibromides and ethyl mercaptan in a 1:3 ratio yield ethyl esters of alkyl bromo thioboric acid (60-70 % yield) which are far more stable than chlorine thioesters and do not change when distilled in vacuum. A similar reaction takes place between phenyl boron dibromide and ethyl mercaptan, resulting in ethyl ester of phenyl dimercaptothioboric acid. The second way of synthesizing alkyl chlorine thioboric acid ester is the exchange reaction between alkyl boron dichlorides and alkyl thioboric acid esters. In this way ethyl ester of n-propyl chlorothioboric acid (yield 50 %) was obtained from an equimolecular mixture of n-propyl boron dichloride and diethyl ester of n-propyl thioboric acid after 20 hr at room temperature. The third way of synthesizing alkyl halogen thioboric acid ester is based on the effect of boron halides on alkyl thioboric acid ester at room temperature. Butyl ester of n-amyl bromo thioboric acid (yield 80 %) was synthesized in this way from butyl ester of n-isoamyl thioboric acid and boron tribromide. The reaction of these esters toward diethyl amine indicates that the halogen atom

Card 2/3

33977

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B117/B138

Orgaroboron compounds. .

organoboron compounds of the type RB(SR')₂ has a higher mobility than the alkyl mercapto group. All reactions were performed in dry nitrogen atmosphere. There are 9 references: 6 Soviet and 3 non-Soviet. The three references to English-language publications read as follows: P. Brindley et al. J. Chem. Soc. 1956, 1540, 824; P. McCusker et al. J. Amer. Chem. Soc. 79, 5182 (1957); E. Abel et al. J. Chem. Soc. [illegible] 2

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: August 18, 1961

Card 3/3

S/844/62/000/000/062/129
D204/D307

AUTHORS: Mikhaylov, B. M. and Kiselev, V. G.

TITLE: The oxidation of ethylene and propylene with oxygen under the action of fast electrons

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 367-373

TEXT: Ethylene oxidized chiefly to peroxides, glycolic aldehyde, HCOOH, $CH \equiv CH$ and CO; small amounts of CH_3CHO, H_2, CO_2 and traces of butylene, CH_2O and CH_3COOH were also found. In an Al reaction maintained at room temperature and initially atm pressure, with C_2H_4/O_2 equal to 1, it was shown that ethylene reacted faster than O_2 on irradiation ($0.2 - 1.7 \times 10^{23}$ ev), especially at the lower doses. The reactor walls behaved as a catalyst until they were covered by the liquid products. Dose magnitude exerted little effect on the

Card 1/3

The oxidation of ....

oxidation yields, for irradiation periods longer than 15 min. Under similar conditions, in oxygen-poor starting mixtures, those processes were favored in which O_2 does not play a primary part; oxygen-rich mixtures led to a fuller oxidation of the olefin. Energy yields were relatively independent of the dose of irradiation and the olefin: O_2 ratio (n). The reaction proceeded similarly in Al steel, glass and brass reactors, (although in the last cases some secondary reactions were affected), and was relatively uninfluenced by changes of temperature (-40 to +80°C). Under similar conditions (Al reactor, room temperature, initially atmospheric pressure, a dose of 0.55×10^{23} ev, n = 1) propylene oxidized mainly to acetol, peroxides, CO and propionaldehyde, with smaller amounts of HCOOH, CH_2O and CO_2. The reaction is analogous to that of ethylene. It is proposed that the initial stage of oxidation comprises the addition of O_2 across the double bond of the activated olefin, to form cyclic peroxides, (I), which then isomerize to glycollic aldehyde or acetol. Acetaldehyde and propionaldehyde form by the reaction of

The oxidation of ...

I with further olefin and CO and HCOOH by the reaction of I with further oxygen. There are 6 figures and 3 tables.

ASSOCIATION: Institut organicheskoy khimii AN SSSR im. N. D. Zelinskogo (Institute of Organic Chemistry AS USSR im. N. D. Zelinskiy)

Card 3/3

35590
S/062/62/000/003/006/014
B117/B144

11 1250
5.2410

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A., and Bubnov, Yu. N.

TITLE: Organoboron compounds. Communication 92. Refractions of the bonds of boron with some elements

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 3, 1962, 413-419

TEXT: Refractions of (B — C), (B — O), (B — N), (B — S), and (B — Cl) bonds were calculated from molecular refractions of various organoboron compounds having regard to hybridization according to Denbigh's method. Where possible, compounds of the type BX_3 were used. Molecular refractions were determined from the Lorentz-Lorenz law. For the bonds B — $C_{aliph.}$ and B — O, the mean value of their refractions was found from molecular refractions of boron trialkyls and trialkyl borates: R_D = 1.93 cm^3 and R_D = 1.61 cm^3, respectively. For B — $C_{arom.}$, a mean value of R_D = 2.76 cm^3 was determined from the molecular refractions of aryl boric acids.

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Organoboron compounds...

Molecular refractions of triamides and N-substituted alkyl-(diamino) borons produced a mean value of 1.97 cm^3 for the refractions of B — N. The mean refraction value for the B — N bond in dialkyl-(amino) borons, their N-substituted and dialkyl boryl hydrazines was 2.01 cm^3. Thus, the mean refraction value of the B — N bonds may be assumed to be 1.98 cm^3. For the B — S bond in thioborates as well as in alkyl- and dialkyl thioboric esters, a mean refraction value of 5.59 cm^3 was determined, which is somewhat higher than the value of 5.20 cm^3 determined for this bond in dialkyl thioboric acids. Various organoboron chlorides were used for calculating the refractions of the B — Cl bond. As the production of these chlorides in pure form is difficult owing to their tendency towards disproportionation and their easy hydrolyzability, the values found showed high fluctuations and produced a mean value of R_D = 6.88 cm^3. There are 13 tables and 27 references: 15 Soviet and 12 non-Soviet. The four most recent references to English-language publications read as follows: P. M. Chistopher, T. J. Tully, J. Amer. Chem. Soc., 80, 6516 (1958); G. F. Hennion, P. A. McCusker, J. V. Marra, J. Amer. Chem. Soc., 80, 3481 (1958) and J. Amer. Chem. Soc. 81, 1768 (1959); D. Aubrey, M. Lappert,

Card 2/2 Inst. Org. Chem. im N.D. Zelinskiy AS USSR

S/062/62/000/004/005/013
B110/B101

5.2410

AUTHORS: Mikhaylov, B. M., and Galkin, A. F.

TITLE: Organo-boron compounds. Communication 95. Synthesis of B-alkyl-B-dialkyl mercapto derivatives of borazol and some of their conversions

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 4, 1962, 619-623

TEXT: The authors had found earlier (Izv. AN SSSR. Otd. khim. n. 1959, 172; ibid. 1961, 371; Dokl. AN SSSR, 127, 571 (1959); ibid. 127, 1023 (1959), that alkyl mercapto derivatives of organo-boron compounds are highly reactive, and often surpass organo-boron halides with respect to synthesis. For this reason, the reaction of organo-metallic compounds with B-trimercapto derivatives of borazol was studied for the purpose of obtaining bifunctional borazol derivatives; the B-trimercapto derivatives had been obtained from lead mercaptides and B-trichloro borazols. 1 mole of n-butyl magnesium chloride with 1 mole of B-tri-n-butyl mercapto borazol (I) gives a 33% yield of B-n-butyl-

APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001034010004-8"

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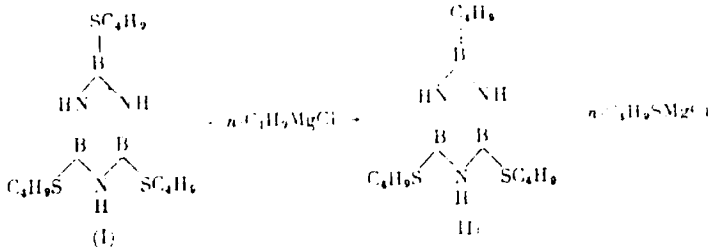
B110/B101

Organo-boron compounds. ...

B-di-n-butyl mercapto borazol (II) (b.p. 115-120°C (0.2 mm Hg), $d_4^{20} = 0.9860$, $n_D^{20} = 1.5065$, MR = 95.33 ($C_{12}H_{30}B_3N_3S_2$)):



The reaction of 1 mole of B-trialkyl mercapto-N-trialkyl borazols (R = CH_3, C_2H_5) with 0.8 moles of n-butyl lithium showed a smoother, stepwise replacement of the alkyl mercapto groups by alkyl radicals. B-alkyl-B-dialkyl mercapto-N-trialkyl borazols were obtained in 62-65% yield:

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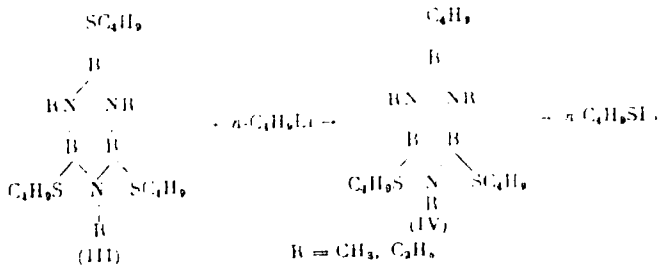
Organo-boron compounds. ...



With the same ratio of reagents and with ethyl lithium, B-ethyl-B-di-n-butyl mercapto-N-triethyl borazol (V) is obtained with a yield of 62.5% (b.p. 161-163°C (0.15 mm Hg), d_4^{20} = 0.9826, n_D^{20} = 1.5080, MR = 113 ($C_{16}H_{38}B_3N_3S_2$)).

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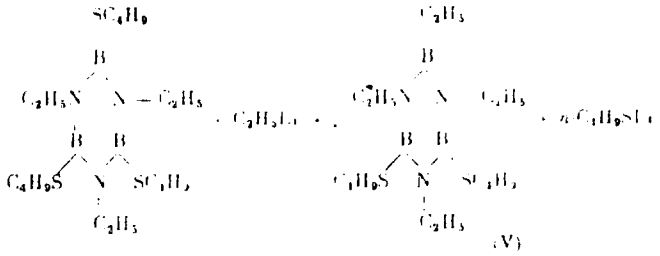
S/062/62/000/004/005/013
B110/B101

Organo-boron compounds. ...



(V)

Like the B-trialkyl mercapto derivatives of borazol, these B-alkyl-B-di-n-butyl mercapto-N-trialkyl borazols can react with various reagents with active hydrogen: 2 moles of CH_3OH with (IV) (R = C_2H_5) give a 58% yield of B-n-butyl-B-dimethoxy-N-triethyl borazol (VI) ($C_{12}H_{30}B_3N_3O_2$) (b.p. 147-150°C (2 mm Hg), d_4^{20} = 0.9565, n_D^{20} = 1.4608, MR = 80.5):

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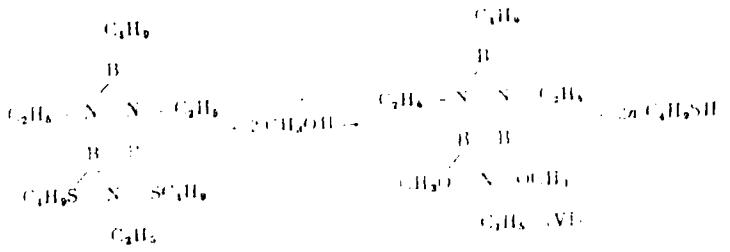
B110/B101

Organo-boron compounds. ...



B-alkyl-[illegible]-alkyl mercapto derivatives of borazol react even more readily with primary and secondary amines: 2 mols of methylamine with (V) or (IV) (R = C_2H_5) give a 73-[illegible] yield of B-ethyl-B-di-(methylamino)-N-triethyl borazol (VII, R = C_2H_5) ($C_{10}H_{28}B_3N_5$) (b.p. 101-103°C (0.3 mm Hg), d_4^{20} = 0.9748, n_D^{20} = 1.4850, MR = 73.8) and B-n-butyl-B-di-(methylamino)-N-triethyl borazol (VII, R = n-C_4H_9)

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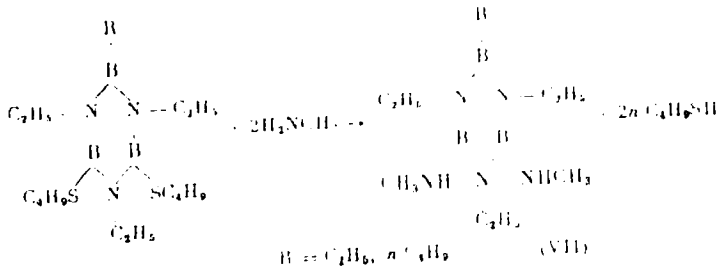
Organo-boron compounds. ...

$(C_{12}H_{32}B_3N_5)$ (b.p. 100-105°C (0.1 mm Hg), d_4^{20} = 0.9557, n_D^{20} = 1.4870, MR = 83.7):



(IV) or (V) (R = C_2H_5) with dimetnyl amine give a 70-75% yield of B-ethyl-B-di-(dimethylamino)-N-triethyl borazol (VIII, R = C_2H_5) $(C_{12}H_{32}B_3N_5)$ (b.p. 88-90°C (0.3 mm Hg), d_4^{20} = 0.9359, n_D^{20} = 1.4830, MR = 86.50) and B-n-butyl-B-di-(dimethylamino)-N-triethyl borazol

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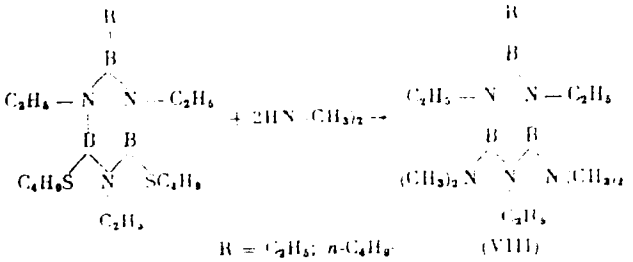
Organo-boron compounds. ...

(VIII, R = n-C_4H_9) ($C_{14}H_{36}B_3N_5$) (b.p. 110-115°C (0.05 mm Hg), d_4^{20} = 0.9333, n_D^{20} = 1.4845):



The English-language reference reads as follows: G. Ryschkewitsch, T. Harris, H. Sisler, J. Amer. Chem. Soc., 80, 4515 (1958).

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S/062/62/000/004/005/013
B110/B101

Organo-boron compounds. ...

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: November 1, 1961

X

Card 8/8

MIKHAYLOV, B.M.; DOROKHOV, V.A.

Organoboron compounds. Report No.96: Reactions of 1,2-diaryldiboranes with primary amines. Izv.AN SSSR Otd.khim.nauk no.4: 623-627 Ap '62. (MIRA 15:4)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boron hydrides) (Amines)

MIKHAYLOV, B.M.; VASIL'YEV, L.S.

Organoboron compounds. Report No.97: Action of diborane on esters of dialkyl boric acids. Izv.AN SSSR Otd.khim.nauk no.4:628-634 Ap '62. (MIRA 15:4)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Boron hydrides) (Boric acid)

37801
S/062/62/000/005/003/008
B110/B101

AUTHORS: Mikhaylov, B. M., and Vasil'yev, L. S.

TITLE: Organoboron compounds. 99. Reaction of tetraalkyl diboranes with boric acid esters

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 5, 1962, 827 - 833

TEXT: In continuation of previous papers by the authors (Izv. AN SSSR. Otd. khim. n. 1961, 531; Dokl. AN SSSR 139, 385 (1961)), the conversion of tetraalkyl diboranes with orthoboric acid esters into alkyl boric acid esters is investigated. Trimethyl, tri-n-butyl, tri-n-heptyl, and tri-n-heptyl borate with tetra-n-propyl diborane and tetra-n-butyl diborane were used in different ratios and under different conditions. After 2.5 hrs in the water bath tetra-n-propyl diborane and tri-n-heptyl borate (1:2) gave rise to the di-n-heptyl ester of n-propylic acid in a yield of 80 %:
$(R_2BH)_2 + 2(R'O)_3B \rightarrow 3RB(OR')_2 + (1/2)(RBH_2)_2$; $R = n\text{-}C_3H_7$; $R' = n\text{-}C_7H_{15}$.
Some alkyl diborane or dialkoxy borane is also formed. In the initial stage of the reaction between tetraalkyl diboranes and orthoborates,
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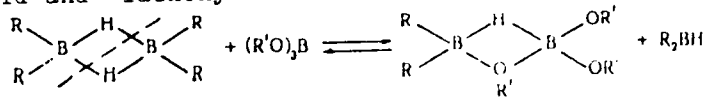
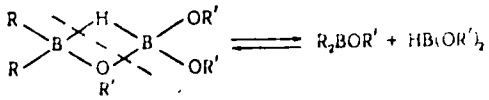
B110/B101

Organoboron compounds. 99. ...

hydrogen is exchanged for the alkoxy group to form the ester of dialkyl boric acid and dialkoxy borane:



(I)



Alkoxy borane is then symmetrized to diborane and borate according to $2HB(OR')_2 \rightleftharpoons 2B(OR')_3 + (1/2)B_2H_6$. Diborane then converts dialkyl boric acid ester into alkyl boric acid ester and dialkyl diborane. Since alkoxy borane possesses a B-H bond, it can also react with the initial tetraalkyl diborane: $(R_2BH)_2 + 2HB(OR')_2 \rightleftharpoons (RBH_2)_2 + 2RB(OR')_2$ or with dialkyl boric acid ester:

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Organoboron compounds. 99. ...

$R_2BOR' + HB(OR') \rightleftarrows RB\begin{matrix}H\\OR'\end{matrix} + RB(OR')_2$. The resulting alkyl alkoxy borane is able to symmetrize to the ester of alkyl boric acid and dialkyl diborane or it may exchange its hydrogen atom for the alkoxy group. The following products were synthesized: (1) n-heptyl ester of di-n-propyl boric acid (b. p. 92 - 97°C/4.5 mm Hg; n_D^{20} = 1.4250), (2) di-n-heptyl ester of n-propyl boric acid (b. p. 120 - 123°C/3.5 mm Hg; n_D^{20} = 1.4292), (3) tri-n-heptyl borate (b. p. 157 - 160°C/3 mm Hg; n_D^{20} = 1.4315), (4) dimethyl ester of n-propyl boric acid (b. p. 58 - 65°C/107 mm Hg; n_D^{20} = 1.3845), (5) di-n-butyl ester of n-propyl boric acid (b. p. 65 - 70°C/3 mm Hg; n_D^{20} = 1.4112), (6) dimethyl ester of n-propyl boric acid (b. p. 45 - 56°C/95 mm Hg; n_D^{20} = 1.3853), (7) di-n-propyl-(phenyl amino) boron (b. p. 76 - 81°C/2 mm Hg; n_D^{20} = 1.5055), (8) dimethyl ester of n-butyl boric acid (b.p. 51 - 54°C/43 mm Hg; n_D^{20} = 1.3950), (9) di-n-butyl-bis-(phenyl

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Organoboron compounds. 99. ...

amino)boron (b. p. 111 - 114°C/4 mm Hg; n_D^{20} = 1.4960), (10) n-butyl-bis-(phenyl amino)boron (b. p. 128 - 132°C/0.08 mm Hg; n_D^{20} = 1.5720).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: December 6, 1961

Card 4/4

S/062/62/000/006/003/008
B117/B101

AUTHOR: Mikhaylov, B. M., and Fedotov, N. S.

TITLE: Organoboron compounds. Communication 100. Reactions of esters of thioboric and organothioboric acids with carbonyl compounds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 6, 1962, 999 - 1001

TEXT: Orthoboric acid esters were shown to react with aldehydes and ketones with formation of thioacetals, thioketals, and boric oxide; di-n-butyl thioketal of acetone (90%) was got besides boric oxide, from a benzene solution of acetone and n-butyl thioborate heated in a water bath (3 hr). Under the same conditions, ethyl thioborate and acetophenone yielded boric oxide and acetophenone diethyl thioketal (82.1%). Ethyl thioborate reacted with benzaldehyde in benzene solution, liberating heat and producing boric oxide and benzaldehyde diethyl thioacetal (91.1%). The reaction of n-butyl phenyl thioborate with acetone yielded phenyl boric anhydride and di-n-butyl thioketal of acetone (86%). The reaction of n-butyl-di-α-naphthyl thio-

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borate with acetone yielded di-α-naphthyl boric anhydride (78.5%), acetone thioketal (8[illegible]), and small amounts of α-naphthyl boric anhydride and naphthalene. The reaction of acetone with diphenyl thioborate gave phenyl boric anhydride (3%) and benzene besides diphenyl boric anhydride (65.4%). The yield of acetone thioketal was only 66.5%. Acetone supplies the hydrogen required for the formation of aromatic hydrocarbons.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: January 11, 1962

Card 2/2

39572
S/062/62/000/007/003/013
B117/B180

5.2410 2220

AUTHORS: Mikhaylov, B. M., and Dorokhov, V. A.

TITLE: Organoboron compounds. Report 101. Synthesis and conversions of complex aryl borane compounds with secondary amines

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1962, 1213 - 1218

TEXT: New aryl borane complexes (dimethyl-phenyl borane, diethyl-amine-p-tolyl borane, and diethyl-amine α-naphthyl borane) were synthesized from 1,2-diphenyl, 1,2-di-p-tolyl, and 1,2-di-α-naphthyl diboranes and the correspondent secondary amines in ether and benzene at -10 - 0°C and their conversions were studied. Diaryl(dialkyl amino)boron and dialkyl amino-borane compounds were obtained from dialkyl amino-aryl borane by pyrolysis at 70 - 150°C. Dialkyl aminoborane reacted with mercaptanes, yielding large amounts of aryl(alkyl-mercapto)dialkyl aminoboron compounds. To complete this reaction, which sets in at room temperature, the mixture has to be heated to 150°C, since the aryl(alkyl mercapto)borane forming in the initial stage reacts with mercaptane to form aryl(alkyl mercapto)di-alkyl amino borane. Aryl(alkyl mercapto)dialkyl aminoboron compounds

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are colorless, easily hydrolyzable liquids which oxidize in air and are converted into aryl-di-(alkyl amino) boron compounds by primary amines. They are more stable than secondary amines. To obtain aryl-di-(alkyl amino) boron compounds, higher-boiling secondary amines must be used, and the mercaptanes and secondary amines forming in the reaction zone must be distilled off.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: January 23, 1962

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39573
S/062/62/000/007/004/013
B117/B180

2220

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A., Shashkova, Ye. M., and Sheludyakov, V. D.

TITLE: Organoboron compounds. Report 102. Monoalkyl mercapto derivatives of borane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1962, 1218 - 1223

TEXT: The reactions of diborane and mercaptanes in ether solution were studied at room temperature. Independent of the component ratio, diborane and methyl mercaptane yielded a solid, storable polymer which dissolves in ether and benzene, and converts into a trimer in a solution of tetrahydrofuran. A viscous, colorless polymer was produced from diborane and ethyl mercaptane, independent of the component ratio. The reaction of diborane with n-propyl and n-butyl mercaptanes only yielded polymers at a ratio of 1 : 2. Trimers of ethyl, n-propyl, and n-butyl mercapto boranes formed spontaneously from the corresponding polymers. The resulting trimers are a new type of organoboron compound. They are very stable, have a cyclic

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